

A microscopic, mechanical derivation of the adiabatic gas relation

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It is shown that the ideal gas adiabatic relation, $PV^\gamma = \text{constant}$, can be derived by considering the motion of a particle bouncing elastically between a stationary wall and a moving wall. © 2004

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I. INTRODUCTION

The simplest form of the adiabatic gas relation is the observation that the temperature of a thermally insulated gas increases when it is compressed and decreases when it is expanded. According to the historical review of this subject by Kuhn,¹ the first publication documenting this behavior was by the Scottish physician William Cullen in the mid-17th century. Experimental observations were summarized by the relation $PV^\gamma = \text{constant}$, where the exponent γ was determined to exceed unity. The deviation of γ from unity is what allowed Sadi Carnot to develop his eponymous cycle. (Apparently Carnot did not have the correct value of γ , but the use of an incorrect value did not affect his fundamental result that heat engine efficiency depends only on inlet and outlet temperatures.)

Serious attempts to develop a theoretical explanation for the adiabatic gas relation were undertaken by Laplace, Poisson, and others in the early 19th century, but no single individual has been identified as being the first to provide the correct theoretical explanation. Since the mid-19th century development of thermodynamics, the adiabatic gas relation has been established from first principles using thermodynamic arguments. The standard thermodynamic derivation is based on considering the temperature change of the gas in a cylinder at constant pressure or constant volume while taking into account specific heats at constant pressure and constant volume.²

The purpose of this paper is to show that the adiabatic gas relation $PV^\gamma = \text{constant}$ is a direct consequence of an important property of periodic mechanical motion, namely adiabatic invariance. Although the word adiabatic is used in both the mechanical and thermodynamic contexts, its meaning in the mechanical context differs from its meaning in the thermodynamic context³ because the concept of heat does not exist in the mechanical context. The derivation presented here provides insight into the fundamental microscopic dynamics underlying adiabaticity. The derivation will first be presented for molecules with no internal degrees of freedom and then extended to molecules with internal degrees of freedom. Two standard properties of an ideal gas will be invoked repeatedly, namely, the properties of an ideal gas occupying a volume V do not depend on the shape of the volume, and collisions cause all properties of an ideal gas to become isotropic.

II. MOLECULES WITHOUT INTERNAL DEGREES OF FREEDOM

A molecule with no internal degrees of freedom may be represented by a point particle. Consider the situation

sketched in Fig. 1 where a point particle bounces back and forth with speed v between two walls. The two walls are denoted as 1 and 2 and are separated by a distance L . Wall 1 is stationary while wall 2 approaches wall 1 with speed u where $u \ll v$. Both u and v are speeds, not velocities, that is, u and v are both positive quantities and leftward motion is denoted by an explicit minus sign. Wall 2 therefore moves in the lab frame with a velocity $-u$.

The critical physical assumption is that the particle bounces elastically from both walls. This microscopic assumption corresponds precisely to the macroscopic adiabatic prescription that the gas is thermally insulated from its surroundings. If particles bounced inelastically from the walls, the temperature of the walls would change and the gas would not be thermally insulated from the external world.

The transformation from the lab frame to the frame of wall 2 requires adding u to the lab frame velocity; the reverse transformation requires subtracting u from the velocity in the frame of wall 2. In the frame of wall 2, the particle approaches wall 2 with velocity $v + u$ and after reflection has the velocity $-v - u$. By transforming back to the lab frame, the lab frame velocity after reflection is $-v - 2u$. The change in the particle speed in the lab frame due to reflection from wall 2 is therefore

$$\Delta v = 2u. \quad (1)$$

Now consider the time for the particle to execute one cycle of bouncing between walls 1 and 2. The distance traveled by the particle on starting from wall 1, reflecting from wall 2, and then returning to wall 1 is $2L$, and so the time to travel this distance is the bounce time

$$t_b = 2L/v. \quad (2)$$

Equation (2) can be used to calculate the change in inter-wall distance during one complete bounce cycle. Because wall 2 is approaching wall 1, this change is negative and is given by

$$\Delta L = -ut_b = -2Lu/v. \quad (3)$$

The presumption $u \ll v$ combined with Eq. (3) implies that $|\Delta L|/L \ll 1$, and so we do not need to take into account changes in either v or in L during a bounce cycle when calculating t_b ; that is, t_b is well-defined even though both L and v change during a bounce cycle.

The combination of Eqs. (1) and (3) gives the relation

$$L\Delta v + v\Delta L = 0, \quad (4)$$

showing that $\Delta(vL) = 0$, or

$$vL = \text{constant}. \quad (5)$$

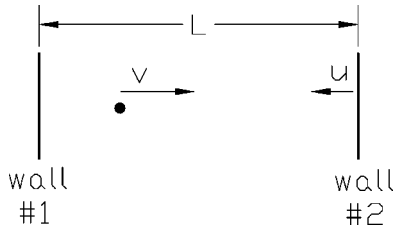


Fig. 1. Wall 2 moves to the left with speed u . The particle has speed v . The distance between the walls is L .

The quantity vL is called an adiabatic invariant^{4,5} and indicates conservation of the phase-space area enclosed by the phase-space trajectory of periodic motion. This invariance is a fundamental property of the periodic motion of Hamiltonian systems in which there exists a slowly changing parameter (the word slowly in our case corresponds to $u \ll v$). Energy is not conserved and scales as $v^2 \sim 1/L^2$.

Now assume that the particle bounces in three dimensions between the walls of a cube with sides of length L , where, for each of the three dimensions, one wall approaches its opposite partner as we have discussed. Thus, the cube decreases in a self-similar fashion as shown in Fig. 2. Equation (5) holds for each of the three dimensions and can be generalized as

$$v_x^2 L^2 = \text{constant}, \quad v_y^2 L^2 = \text{constant}, \quad v_z^2 L^2 = \text{constant}. \quad (6)$$

Hence,

$$v^2 L^2 = (v_x^2 + v_y^2 + v_z^2) L^2 = \text{constant}. \quad (7)$$

A large number of non-interacting particles in such a cube can be considered as an ideal gas with temperature $T \sim \langle v^2 \rangle$ where $\langle \dots \rangle$ denotes an average over all the particles. The average of Eq. (7) over all particles thus gives

$$TL^2 = \text{constant}. \quad (8)$$

Because the volume of the cube is $V = L^3$, Eq. (8) becomes

$$TV^{2/3} = \text{constant}. \quad (9)$$

The ideal gas law gives the relation

$$PV = NkT, \quad (10)$$

where P is the pressure, N is the number of particles, and k is Boltzmann's constant. If we use Eq. (10) to substitute for T in Eq. (9), we obtain the adiabatic relation

$$PV^{5/3} = \text{constant}. \quad (11)$$

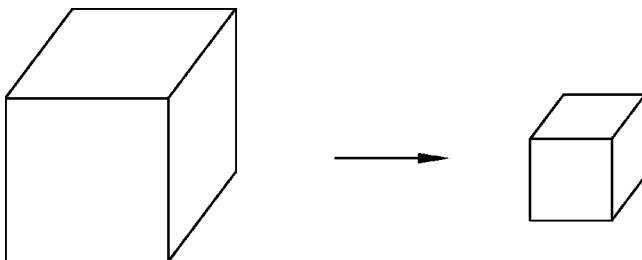


Fig. 2. A cube with sides of length L undergoing a self-similar decrease in volume.

Equation (11) is the sought-after relation, but the derivation has two important restrictions: the cube dimensions changed in a self-similar fashion as in Fig. 2 and the particles were assumed to be non-interacting.

We now repeat the derivation, but this time allow for collisions between particles and also for non-self-similar changes in the dimensions of the volume. As before, the volume is assumed to be thermally isolated from the surroundings, which means that all reflections from the walls are energy-conserving in the frames of the respective walls from which reflection occurs. The combined assumptions of thermal isolation and existence of interparticle collisions means that the final state after an arbitrary change in the linear dimensions of the system is independent of how the change was made. Thus, we are free to choose any sequence of steps we wish when going from an initial state to some specified final state, provided that our two assumptions stated above hold. The following discussion presents a sequence chosen to elucidate the microscopic physics.

We start with a system that has an arbitrary initial shape, initial volume V_0 , initial temperature T_0 ; we want to determine the temperature T when the volume changes to V . We first deform the shape of the volume V_0 as shown in Fig. 3(a) so that the volume becomes rectangular with linear dimensions L_{x0} , L_{y0} , and L_{z0} with $V_0 = L_{x0}L_{y0}L_{z0}$. This shape deformation at constant volume does not change the initial gas temperature T_0 because ideal gas properties are independent of the shape of the volume. Further, because the linear dimensions are arbitrary, we set L_{x0} sufficiently small that the bounce time in the x direction is shorter than the nominal interparticle collision time τ_c , that is, we set L_{x0} such that $2L_{x0}/v \ll \tau_c$. Thus, particles bounce many times in the x direction before they make a collision with another particle.

Next we decrease just the x dimension as shown in Fig. 3(b). Because $dv_x = -v_x dL_x/L_x$, we may write

$$dv_x^2 = -2v_x^2 \frac{dL_x}{L_x}. \quad (12)$$

However, because only the x dimension is being changed, $V \propto L_x$, and so this collisionless change can be written as

$$dv_x^2 \Big|_{\text{collisions}}^{\text{no}} = -2v_x^2 \frac{dV}{V}, \quad (13a)$$

$$dv_y^2 \Big|_{\text{collisions}}^{\text{no}} = 0, \quad (13b)$$

$$dv_z^2 \Big|_{\text{collisions}}^{\text{no}} = 0. \quad (13c)$$

Only the x -direction kinetic energy changes because the only dimension that is being changed is L_x . Because there are no collisions, the y and z directions are decoupled from the x direction, and so there are no changes in the y - or z -direction kinetic energies.

After this decrease, we then wait a few collision times so that collisions have a chance to equilibrate the change in kinetic energy among the three directions. After collisions have shared the change in the x -direction kinetic energy among all three dimensions, we obtain

$$dv_x^2 \Big|_{\text{collisions}}^{\text{after}} = \frac{1}{3} dv_x^2 \Big|_{\text{collisions}}^{\text{no}}, \quad (14a)$$

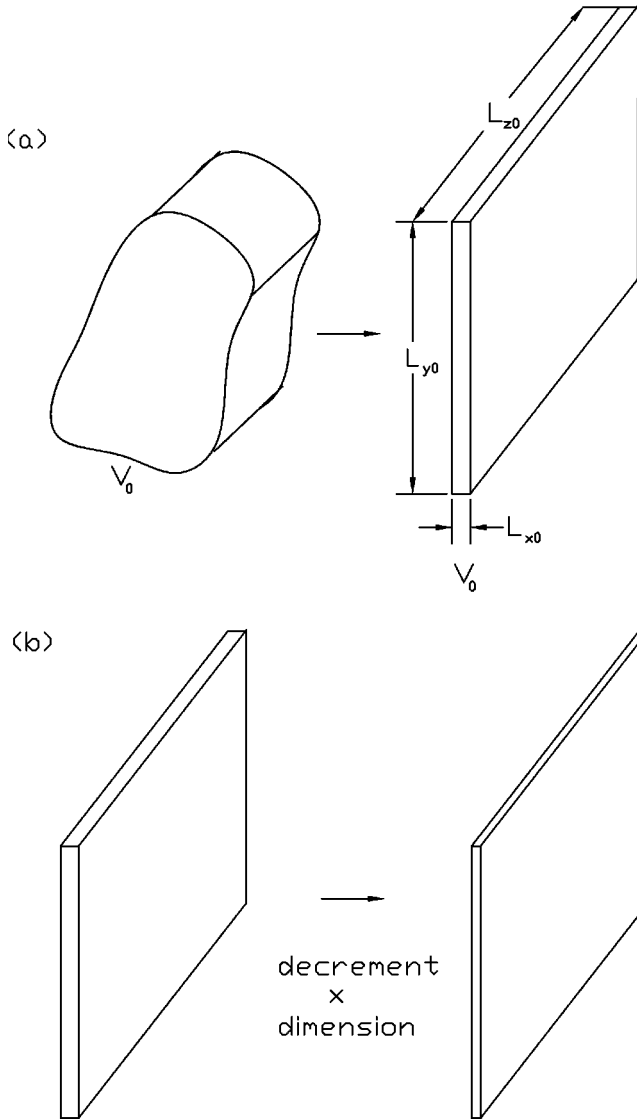


Fig. 3. (a) Change of shape of the gas has no effect when the volume is kept constant; the x dimension is arranged to be so small so that the bounce time in the x direction is less than the collision time. (b) Decrease of x dimension only so that the instantaneous volume is proportional to L_x .

$$dv_y^2|_{\text{after collisions}} = \frac{1}{3} dv_x^2|_{\text{no collisions}}, \quad (14b)$$

$$dv_z^2|_{\text{after collisions}} = \frac{1}{3} dv_x^2|_{\text{no collisions}}. \quad (14c)$$

The combined process of decreasing x and then waiting for collisions to equilibrate the energy gives, using Eqs. (13a) and (14a),

$$dv_x^2 = -\frac{2}{3} v_x^2 \frac{dV}{V}, \quad (15)$$

or, upon integrating,

$$v_x^2 V^{2/3} = \text{constant}. \quad (16)$$

Because the collisions have equilibrated energy amongst the three dimensions of motion, v^2 scales the same as v_x^2 and because T scales as v^2 , we again obtain Eq. (9), which again leads to Eq. (11). Once the system has attained its desired

final volume, it can be deformed at constant volume into whatever shape is desired. Thus, the relation $PV^{5/3} = \text{constant}$ holds for any change in the volume and any shape if there are collisions and if the system is thermally isolated.

III. INTERNAL DEGREES OF FREEDOM

The analysis can now be extended to rigid diatomic and polyatomic molecules. As is well known, a rigid diatomic molecule has two additional degrees of freedom due to rotational motion relative to the center of mass (there is negligible rotational energy about the axis connecting the two atoms comprising the molecule). On the other hand, a polyatomic molecule has three additional rotational degrees of freedom because it can rotate in all three directions about the center of mass. We let n be the number of degrees of freedom so $n=3$ for a monatomic molecule as discussed in Sec. II, $n=5$ for a diatomic molecule, and $n=6$ for a polyatomic molecule. The term “degrees of freedom” is defined as the number of ways that collisions can share an increment in kinetic energy supplied to one direction of motion amongst all possible types of motions of a molecule. We define T_x, T_y, T_z as the kinetic energy due to center of mass motion in the x, y, z directions of a diatomic or polyatomic molecule, that is,

$$T_x = \frac{M}{2} v_x^2, \quad T_y = \frac{M}{2} v_y^2, \quad T_z = \frac{M}{2} v_z^2, \quad (17)$$

where M is the molecular mass and v_x, v_y , and v_z are center of mass velocities. For a diatomic molecule, we define I_1 and I_2 as the additional kinetic energies due to rotational motions relative to the center of mass for the two allowed degrees of freedom of a diatomic molecule. For a polyatomic molecule we similarly define I_1, I_2, I_3 as the kinetic energies of the three allowed degrees of freedom due to rotational motions relative to the center of mass. Consider now decreasing L_x on a time scale shorter than the collision time for a diatomic molecule. In this case, Eqs. (13a)–(13c) become

$$dT_x|_{\text{no collisions}} = -2T_x \frac{dV}{V}, \quad (18a)$$

$$dT_y|_{\text{no collisions}} = 0, \quad (18b)$$

$$dT_z|_{\text{no collisions}} = 0, \quad (18c)$$

$$dI_1|_{\text{no collisions}} = 0, \quad (18d)$$

$$dI_2|_{\text{no collisions}} = 0. \quad (18e)$$

After the collisionless decrease, we wait for collisions to equilibrate the change in kinetic energy amongst the five degrees of freedom and so obtain

$$dT_x|_{\text{after collisions}} = -\frac{2}{5} T_x \frac{dV}{V}, \quad (19a)$$

$$dT_y|_{\text{after collisions}} = -\frac{2}{5} T_x \frac{dV}{V}, \quad (19b)$$

$$dT_z|_{\text{after collisions}} = -\frac{2}{5} T_x \frac{dV}{V}, \quad (19c)$$

$$dI_1|_{\text{after collisions}} = -\frac{2}{5}T_x \frac{dV}{V}, \quad (19d)$$

$$dI_2|_{\text{after collisions}} = -\frac{2}{5}T_x \frac{dV}{V}. \quad (19e)$$

If we repeat this process of decreasing collisionlessly, then waiting for collisions to equilibrate the energy among the five degrees of freedom, T_x is seen to be governed by

$$dT_x = -\frac{2}{5}T_x \frac{dV}{V}, \quad (20)$$

which may be integrated to give

$$T_x V^{2/5} = \text{constant}. \quad (21)$$

Because the temperature T scales as T_x , we have

$$TV^{2/5} = \text{constant}. \quad (22)$$

Clearly, Eq. (22) can be generalized to the form

$$TV^{2/n} = \text{constant}, \quad (23)$$

where $n=3$ for a monatomic molecule, $n=5$ for a diatomic molecule, and $n=6$ for a polyatomic molecule. If we combine Eq. (23) with Eq. (10), we obtain the general result

$$PV^\gamma = \text{constant}, \quad (24)$$

where

$$\gamma = \frac{2+n}{n}. \quad (25)$$

Thus $\gamma=5/3$ for a monatomic molecule, $\gamma=7/5$ for a diatomic molecule, and $\gamma=4/3$ for a polyatomic molecule.

IV. DISCUSSION

Adiabatic gas behavior is closely related to the one-dimensional periodic motion of a particle in a slowly changing system. This motion satisfies the fundamental relation, $vL = \text{constant}$, which is a limiting form of the general adiabatic conservation rule for slowly changing periodic motion of a Hamiltonian system,⁴ namely that $\oint p dq = \text{constant}$, where p and q are generalized coordinates and the integral is over one period of oscillation. The $vL = \text{constant}$ relation is the basis for Fermi acceleration,⁶ the process by which cosmic charged particles can be accelerated to extreme energies when they bounce back and forth between converging magnetic fields playing the role of converging walls.

As mentioned, it is the *elastic* bouncing of the particle from the walls that makes the process adiabatic; if the bouncing were inelastic, the wall would heat up in which case the gas would not be thermally isolated. The $vL = \text{constant}$ relation also is intrinsic to the Wentzel–Kramers–Brillouin (WKB) approximation of a simple harmonic oscillator, for example, a pendulum with slowly varying length or equivalently the Schrödinger equation for a particle in a slowly changing potential well. When applied to the pendulum problem, the WKB approximation involves solving the equation $d^2x/dt^2 + \omega^2(t)x = 0$, where $\omega(t)$ is a time-dependent

frequency.⁷ The frequency $\omega(t)$ is essentially the inverse of the bounce time defined in Eq. (2) and so $\omega(t) \sim t_b^{-1} \sim v/L$. Because $vL = \text{constant}$, it is seen that $v^2/\omega(t) \sim \text{constant}$ and so the harmonic oscillator energy increases in proportion to the frequency. Energy is not conserved, but the ratio of energy to frequency is.

When there are non-self-similar volumetric changes and collisions, our derivation of the adiabatic gas law from mechanical considerations requires separating the process into a sequence of infinitesimal steps where each step has two successive sub-steps, namely a one-dimensional change in volume which adiabatically (in the mechanical sense) changes the center of mass kinetic energy of the changed dimension only, and then a collision-mediated sharing of this energy change among all allowed degrees of freedom. This point of view clearly shows why diatomic and polyatomic molecules have a different γ from monatomic molecules.

Finally, it is worth addressing a possible confusion regarding whether adiabatic processes are fast or slow: adiabatic processes are characterized both ways, depending on the context. In order for an adiabatic invariant to exist in the context of classical mechanics, the system must change slowly, that is, the change of the bounce time per bounce must be small compared to the bounce time.⁸ From the thermodynamic point of view, an adiabatic process must be fast compared to the time for heat to leave the system, that is, the change in the dimensions of the configuration must occur faster than the time for walls to heat up due to inelasticities of the reflecting particles. Possible confusion is avoided by realizing that adiabatic processes must be slow compared to particle bounce times so as to satisfy the $u \ll v$ assumption, but fast compared to heat loss times so as to satisfy the assumption that the particle bounces elastically from the wall.

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¹T. S. Kuhn, "The caloric theory of adiabatic compression," *Isis* **49**, 132–140 (1958).

²See for example, R. A. Serway and R. J. Beichner, *Physics for Scientists and Engineers* (Brooks/Cole, Pacific Grove, CA, 2000), 5th ed., Vol. 1, p. 650.

³The word adiabatic means "at constant heat" in the context of thermodynamics and thus indicates that the system is thermally insulated from the external world. Adiabatic does not mean that energy is conserved within the system and adiabatic processes typically involve energy changes of the system.

⁴L. D. Landau and E. M. Lifshitz, *Mechanics* (Pergamon, Oxford, 1969), 2nd ed., p. 154.

⁵T. G. Northrop, *The Adiabatic Motion of Charged Particles* (Interscience, New York, 1963), p. 47.

⁶E. Fermi, "Galactic magnetic fields and the origin of cosmic radiation," *Astrophys. J.* **119**, 1–6 (1954).

⁷For a discussion of this in the context of the Schrödinger equation, see, for example, D. J. Griffiths, *Introduction to Quantum Mechanics* (Prentice–Hall, Upper Saddle River, NJ, 1995), p. 274.

⁸This slowness requirement is essentially the WKB criterion for a variable-length pendulum. See, for example, Ref. 4.